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(54) Name of invention

Waste Treatment Material

(57) Summary

[Purpose] Provide a treatment material that will control the liquation of harmful heavy metals contained in waste, and also has desirable preservation stability.

[Structure] Principal structure components of solid acids such as  $Al(SO_4)_3$ , aluminum silicate,  $AlPO_4$ , and chemicals that are consolidation inhibitors, such as active clay, active alumina, Ca stearate, and silica gel; reducing agent, allophone, bentonite, zeolite, activated carbon, and others may be added to the waste treatment material that is kneaded with the stray ash to dispose of waste matter.

[Effect] Able to stabilize harmful heavy metals contained in industry waste, and also has desirable preservation stability.

[Extent of patent claim application]

[Claim 1] A waste treatment material characterized by the principal structure components of solid acids and consolidation inhibitors.

[Claim 2] A waste treatment material stated in Claim 1, that is characterized by a choice made of one or more of the following as solid acids: natural clay minerals such as acid clay, clarite, bentonite, kaolin, fuller's earth, montmorillonite, phlorizin; sulfuric acid, phosphoric acid, malonic acid, and others adhered to silica gel and alumina; solidifying acid such as phosphoric acid, calcinated synthetic substance from diatomite and phosphoric acid with quartz grain as the carrier; cation substitution resin; ZnO and  $Al_2O_3$  or these after heat treatment,  $TiO_2$  or this after heat treatment,  $CeO_2$  or this after heat treatment,  $As_2O_3$ ,  $V_2O_5$ , and  $SiO_2$  or these after heat treatment,  $Sb_2O_5$ ,  $CaSO_4$ , and  $MnSO_4$  or these after heat treatment,  $NiSO_4$  or this after heat treatment,  $CuSO_4$  or this after heat treatment,  $CoSO_4$  and  $CdSO_4$  or these after heat treatment,  $SrSO_4$  and  $ZnSO_4$  or these after heat treatment,  $MgSO_4$  and  $FeSO_4$  or these after heat treatment, heat treated  $BaSO_4$ ,  $KHSO_4$ ,  $K_2SO_4$ ,  $(NH_4)_2SO_4$ ,  $Al_2(SO_4)_3$ ,  $Fe_2(SO_4)_3$ ,  $Cr_2(SO_4)_3$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $Bi(NO_3)_3 \cdot 5H_2O$ ,  $Zn(NO_3)_2 \cdot 6H_2O$ , and  $Fe(NO_3)_3 \cdot 9H_2O$ ,  $CaCO_3$ , Zr phosphate, Ti phosphate,  $AlPO_4$ ,  $PbCl_2$ , and  $HgCl_2$  or these after heat treatment,  $AlCl_3$  or this after heat treatment,  $SnCl_2$  or this after heat treatment,  $CaCl_2$ ,  $AgCl_2$ ,  $H_2WO_4$ ,  $AgClO_4$  and ZnS or these after heat treatment, inorganic chemicals such as CaS,  $Mg(ClO_4)_2$ , and aluminum silicate.

[Claim 3] A waste treatment material stated in Claim 1, that is characterized by a choice made of one or more of the following as solid acids:  $Al_2(SO_4)_3$ , aluminum silicate, or  $AlPO_4$ .

[Claim 4] A waste treatment material stated in any of the above Claims 1 through 3, that is characterized by pulverized solid acids.

[Claim 5] A waste treatment material stated in Claim 1, that is characterized by a 1 to 20 weight percentage of compound volume of consolidation inhibitors within the treatment material.

[Claim 6] A waste treatment material stated in Claim 1, that is characterized by a choice made of one or more of the following as consolidation inhibitors: silica gel, diatomite, bentonite, active clay, stearate, alkylamine acetate, palm oil, acid clay, active bauxite, active alumina, acrylic resin, polyvinyl acetate, polyvinyl butyrol, paraffin, sulfur, Ca carbonate, basic Mg carbonate, Ca phosphate, kalion (*kaolin?*), talc, ferric ammonium citrate, K sulfate, and Al silicate.

[Claim 7] A waste treatment material stated in Claim 6, that is characterized by pulverized inorganic matter as consolidation inhibitors.

[Claim 8] A waste treatment material stated in Claim 6 that is characterized by consolidation inhibitors that are organic matter and coat the pulverized solid acid by spraying or soaking.

[Claim 9] A waste treatment material stated in Claim 1 or 5 that is characterized by a choice made of one or more of the following as consolidation inhibitors: active clay, active alumina, Ca stearate, and silica gel.

[Claim 10] A waste treatment material stated in any of the above Claims 1 through 9, that is characterized by the addition of a reducing agent, allophane, and bentonite as auxiliary agents.

[Claim 11] A waste treatment material stated in Claim 10 that is characterized by a choice made of one or more of the following as reducing agents: sodium thiosulfate, thiourate, iron (II) chloride, nitrium sulfite, and hydrosulfite.

[Claim 12] A waste treatment material stated in Claim 10 that is characterized by a reducing agent that is sodium thiosulfate or thiourate.

[Claim 13] A waste treatment material stated in Claim 10 that is characterized by an addition of zeolite or activated carbon.

[Claim 14] A waste treatment method that is characterized by mixing and kneading alkaline stray ash with the waste treatment material, mainly consisting of solid acids and consolidation inhibitors, to which water may be added if necessary.

[Claim 15] A waste treatment method that is characterized by a choice made of one or more of the following as solid acids:  $Al_2(SO_4)_3$ , aluminum silicate, or  $AlPO_4$ .

[Claim 16] A waste treatment method stated in Claim 14, that is characterized by a 1 to 20 weight percentage of compound volume of consolidation inhibitors within the treatment material.

[Claim 17] A waste treatment method stated in Claim 14 or 16 that is characterized by a choice made of one or more of the following as consolidation inhibitors: active clay, active alumina, Ca stearate, and silica gel.

[Claim 18] A waste treatment method stated in any of the above Claims 14 through 17, that is characterized by the addition of a reducing agent, allophane, and bentonite as auxiliary agents.

[Detailed explanation of invention]

[0001]

[Utilization area within the industry] This invention is in regards to a waste treatment material that is effective in disposing waste containing harmful heavy metals in a stable manner.

[0002]

[Former technology] Presently, when industrial waste containing harmful heavy metals is disposed of, a method, in which the liquation of harmful heavy metals is prevented and stabilized by mixing with cement, adding water and kneading, then letting cure until hardened, is used. However, this current treatment method of simply solidifying in cement has various problems, and there is threat of a secondary pollution without limiting use. Also, in cases of stray ash caught at city garbage incinerators, harmful heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), chrome (Cr), and copper (Cu) are contained, but this stray ash is currently being mixed and buried with the bulk ash or solidified in cement. However, there is a problem with Pb liquation even if it is solidified in cement. In addition, in order to capture hydrochloride gas that occurs at incineration slaked lime and quicklime are added; and as these remain in the stray ash, lead liquation can not be restrained and is becoming a large problem. In response to this type of stray ash, a chelator has been in trial use, but depending on the type of stray ash, especially with that having a high alkaline level and high lead content, more than 6% of the stray ash weight must be added in order for some to be restrained lower than the regulation value, and running costs may be a significant burden. In the future, the treatment of untreated stray ash in landfills will be restricted by law and a treatment method in which stabilization of harmful heavy metals to prevent liquation was desired.

[0003]

[Issues targeted by this invention] In consideration of the current industrial waste and stray ash treatment situation, the inventors researched and developed an inexpensive waste treatment material, and found that a waste treatment material that is effective in stabilizing waste containing harmful heavy metals, is able to stabilize so the harmful heavy metals contained in the above alkaline stray ash released from the incinerators does not re-liquate, and that is made up of solid acids is desirable. However, for reasons unknown, if this waste treatment material made up of solid acids is left as is, it at times hardens (consolidates) and there are problems with the preservation stability of the treatment material. For example, a problem point was that handling became very difficult if the length of time when it is stored as product or left in hoppers for use is was lengthy and it consolidated. Therefore, this invention aims to provide a waste treatment material that is able to stabilize the harmful heavy metals contained in the alkaline stray ash released from the abovementioned incinerators so there is no re-liquation, and also improves on the preservation stability of the treatment material.

[0004]

[Steps for achieving target] As a result of diligently working toward solving this type of problem, the inventors achieved the target by finding this waste treatment material. That is, the content of this invention is a waste treatment material mainly consisting of solid acids and consolidation inhibitors.

[0005] The following are examples of solid acids utilized in this invention: (a) natural clay minerals such as acid clay, clarite, bentonite, kaolin, fuller's earth, montmorillonite, and phlorizin, (b) sulfuric acid, phosphoric, and malonic acid adhered to silica gel or alumina, phosphoric acid with quartz grain as the carrier, calcinated synthetic substance from diatomite and phosphoric acid, (c) cation substitution resin, (d) inorganic chemicals such as ZnO, Al<sub>2</sub>O<sub>3</sub> (or this after heat treatment: hereinafter noted with \*), TiO<sub>2</sub>\*, CdO<sub>2</sub>\*, As<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>\*, Sb<sub>2</sub>O<sub>5</sub>, CaSO<sub>4</sub>, MnSO<sub>4</sub>\*, NiSO<sub>4</sub>\*, CuSO<sub>4</sub>\*, CoSO<sub>4</sub>, CdSO<sub>4</sub>\*, SrSO<sub>4</sub>, ZnSO<sub>4</sub>\*, MgSO<sub>4</sub>, FeSO<sub>4</sub>\*, heat treated BaSO<sub>4</sub>, KHSO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O, Bi(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O, CaCO<sub>3</sub>, Zr phosphate, Ti

phosphate,  $\text{AlPO}_4$ ,  $\text{PbCl}_2$ ,  $\text{HgCl}_2^*$ ,  $\text{CuCl}_2^*$ ,  $\text{AlCl}_3^*$ ,  $\text{SnCl}_2^*$ ,  $\text{CaCl}_2$ ,  $\text{AgCl}_2$ ,  $\text{H}_2\text{WO}_4$ ,  $\text{AgClO}_4$ ,  $\text{ZnS}^*$ ,  $\text{CaS}$ ,  $\text{Mg}(\text{ClO}_4)_2$ , and aluminum silicate.

[0006] To choose solid acids, it is desirable that an inexpensive solid acid be chosen according to the invention's main purpose, but it is also necessary to take the following points into consideration.

(1) The component itself of the chemical compounds of Pb, As, Hg, Cd may at times fall into the liquation regulated harmful heavy metals, and it is necessary to confirm through liquation trials at the time of use.

(2) As the best solid acid may vary depending on the waste to be disposed, it is necessary to confirm through liquation trials at the time of use.

[0007] Taking these points into consideration, a favorable condition would be to use  $\text{Al}_2(\text{SO}_4)_3$ , aluminum silicate, and  $\text{AlPO}_4$  as the solid acids used in this invention. Also, a pulverized form of the solid acid is preferred for its reactive nature. Furthermore, the utilization of various solid acids depending on its purpose is within the extent of this invention.

[0008] Furthermore, it can not be said that all of the abovementioned solid acids will consolidate, and it is not always the composition, but also surface area, surface condition, and other elements, that decides whether it will consolidate or not, so separating solid acids that require consolidation inhibitors is difficult. Therefore, taking the consolidation prevention of this invention into definite consideration, it is a good idea to use a consolidation inhibitor in the invention even if the solid acid does not have an easily consolidated nature.

[0009] The following are examples of consolidation inhibitors utilized in this invention: silica gel, diatomite, bentonite, active clay, stearate, alkylamine acetate, palm oil, acid clay, active bauxite, active alumina, acrylic resin, polyvinyl acetate, polyvinyl butyrol, paraffin, sulfur, Ca carbonate, basic Mg carbonate, Ca phosphate, kaolin (*kaolin?*), talc, ferric ammonium citrate, K sulfate, and Al silicate. As consolidation inhibition effects are seen in inorganic substances when mixed in powder form, but the effect is seen in most organic substances when pulverized solid acids are coated, it is necessary to coat the surface of the pulverized solid acids by spraying and soaking. Of the abovementioned consolidation inhibitors, active clay, active alumina, Ca stearate, and silica gel are effective due to their cost, ease of procurement for manufacturing, and consolidation inhibiting effect especially, and are favorable examples. Also, it is within the extent of this invention to utilize 2 or more of the above consolidation inhibitors simultaneously. Furthermore, some consolidation inhibitor substances, such as bentonite and acid clay, are also noted as solid acids and the utilization of these substances, from the liquation prevention capacity point of view, is favorable.

[0010] Choice and usage amount of the abovementioned consolidation inhibitors must be suitably chosen for the solid acid type and quantity in the waste treatment material, but it is also important to ensure that the effects of consolidation inhibiting are enough and that liquation prevention is not hampered. Taking these points into consideration, consolidation inhibitors are added to the extent of typically 1 to 20 weight percentage most of the time.

[0011] In addition to the abovementioned chemical compounds, reducing agents, allophane, bentonite may be added in the invention. Examples of reducing agents are: sodium thiosulfate, thiourate, iron (II) chloride, iron (II) sulfate, nitrium sulfite, and hydrosulfite. Of these, the sodium thiosulfate and thiourea are more favorable. It is thought that, with the waste treatment material of this invention, when chemical compounds such as the above are included, it is possible to bring about a reducible state to the treatment material by mixing and kneading the waste containing harmful heavy metals with the reducing agents. Also, it is thought that allophane and bentonite have adhesive natures. Zeolite and activated carbon can be added to the invention as well, to increase the effect. Therefore, a higher level of stability can be expected from the heavy metals by adding chemical compounds from the about group as auxiliary agents to the treatment material mainly consisting of solid acids and consolidation inhibitors.

[0012] Next, the production method of this invention's waste treatment material will be explained. This treatment material, of mainly solid acids or consolidation inhibitors will be pre-mixed. There is no specific order or restrictions regarding mixing and its method. In regards to storage of the treatment material, it is best to avoid mixing with water, in the same manner as with cement.

[0013]

[Function] It is generally known that Pb in waste incinerator stray ash easily liquates under the alkaline atmosphere, but as city garbage incinerators blow in slaked lime during operation to control chlorine gas, and Pb liquation amounts are especially high in the electric dust chamber captured stray ash and bug filter captured stray ash under these operation conditions. In regards to these types of stray ash, the treatment material of this invention was developed based on the idea to bring the alkaline atmosphere to a more neutral state by decreasing Pb liquation; however, although the expected control effect in Pb liquation value was verified, it did not always decrease and the function was not always clearly seen. Although it is not always clear in regards to the consolidation inhibiting mechanism of the consolidation inhibitor, it can be speculated that it is due to the addition of buffer effect, moisture absorption effect, moisture proofing effect, or fluidity.

[0014]

[Effects of the invention] When industrial waste containing harmful heavy metals and EP ash or bug ash (especially EP ash and bug ash containing slaked lime and quicklime) released from city garbage incinerators are treated utilizing this invention of waste treatment material, harmful heavy metals – especially Pb – are stabilized effectively and liquation amount decreased, and is very effective in stabilizing treatment, in addition to which, this treatment material has superior preservation stability and ease of handling.

[0015]

[Example of application] Using the following examples of application and examples of comparison, this invention will be explained further, however, use is not limited to these examples.

[0016] (Comparison 1) The Pb content measurement result of bug filter captured stray ash generated in the city garbage incinerating facility is shown in Table 1. Using this stray ash untreated, liquation testing was done in accordance with the Environmental Agency Announcement #13 (Japan), and the Pb liquation amount was 240ppm, and PH was 12.6.

[0017]

[Table 1]

Pb measurement in stray ash	
Component	Weight Percentage (%)
Pb	0.9

[0018] (Comparison 2) When approximately 30g of water is added to a mixture of 50g of the stray ash from the above Comparison 1 and 15g of Type I Portland cement, cured for 7 days, and liquation tested in accordance with Environmental Agency Announcement #13 (Japan), the Pb liquation amount was 10ppm.

[0019] (Comparison 3) Al sulfate (Yashiro Chemical-made) was utilized as a stabilizing treatment material. Here, 2 Al sulfates from 2 different production lots of the same manufacturing process were used; and testing and test results for each Al sulfate will be called Comparison 3-1 and 3-2 respectively. When approximately 30g of water is added to a mixture of 50g of the stray ash from the above Comparison 1 and 7.5g of the above treatment material, the kneaded mixture rests for 1 day, and liquation tested in accordance with Environmental Agency Announcement #13 (Japan), the results are as shown in Table 2. Also, a consolidation test was conducted by putting approximately 200g of the treatment material in a 500ml poly container, leaving it for 3 days and 18 days with a 5kg of load weight on top, then straining it through a 2mm mesh screen, and measuring the amount of treatment material is left on top of the screen (lumps). Results are shown on Table 2 with the ratio (%) between the lump amount and initial weight (lower ratio is better).

[0020] Comparing Comparison 3-1 and 3-2, it can be seen that even in Al sulfate from the same manufacturer, different lots may give largely different results in consolidation testing. It is thought that this may be the result of subtle influences that production conditions and storage conditions may have had on the surface condition, but details are currently unknown. The examples of application given below use the same Al sulfate as Comparison 3-2, that is, the Al sulfate from the lot that is more likely to consolidate, in order to make clear this invention's effects.

[0021] (Example 1-3) A stabilizing treatment material was produced by combining and mixing Al sulfate (Yashiro Chemical-made) and active clay (Wako Pure Chemical-made) at a ratio of 10:10 by weight. When approximately 30g of water is added to a mixture of 50g of the stray ash from the above Comparison 1 and 8.25g of this treatment material, the kneaded mixture rests for 1 day, and liquation tested in accordance with Environmental Agency Announcement #13 (Japan). These liquation test results and the consolidation test results for the abovementioned treatment material are shown in Table 2 as Example 1. A similar test, in the same manner as Example 1, was conducted using active alumina (Wako Pure Chemical-made) instead of active clay. Liquation test and consolidation test results are shown in Table 2 as Example 2. In addition, a similar test, in the same manner as Example 1, was conducted using Al silicate (Wako Pure Chemical-made) instead of Al sulfate. Liquation test and consolidation test results are shown in Table 2 as Example 3.

[0022]

[Table 2]

	Treatment Material	Consolidation Test Result (%)		Liquation Test Result
		3 days rest	18 days rest	Pb (ppm)
Comparison 1	-----	-----	-----	240
Comparison 2	cement	-----	-----	10
Comparison 3-1	Al sulfate	0	0	N. D.
Comparison 3-2	Al sulfate	17	20	N. D.
Example 1	Al sulfate + active clay	0	0	N. D.
Example 2	Al sulfate + active alumina	0	0	N. D.
Example 3	Al silicate + active clay	0	0	N. D.

N. D.: Below detection limit of 0.1ppm

[0023] The comparisons and examples in Table 2 above show that the former method seen in Comparison 2 may largely restrict Pb liquation amount through cement treatment compared to the untreated Comparison 1, but Comparisons 3-1 and 3-2, which used Al sulfate as the solid acid, was able to reduce it to below the detection limit (lower than 0.1ppm), and it is clear the use of solid acids is significant. However, when using the abovementioned solid acids, problems may arise with consolidation as in Comparison 3-2. In response to this, Examples 1, 2, and 3 that utilize consolidation inhibitors had liquation prevention results similar to Comparison 3, in addition to having good results for the treatment material consolidation test, and clearly show the effect of this invention. Through all of the above, the capacity of harmful heavy metals liquation prevention and consolidation inhibition effect (preservation stability) of this invention's treatment material is shown, and the effects of this invention's waste treatment material is made clear. Furthermore, for the 50g of ash acting as solid acid contained in the treatment material in Comparison 3 and Example 1, 2, and 3, the weight was set to be 7.5g.

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